

# Effect of Calcium Nitrite Corrosion Inhibitor On Concrete

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**Abstract-** Even the history of concrete has been centuries old, the theories of concrete is not clearly understood. The conventional concrete still possess lot of problems regarding sustainability, durability and mechanical properties. Similarly the corrosion is one of the major issues in the concrete. To delay corrosion in concrete the corrosion inhibitors are widely used now. In this present investigation the effect of calcium nitrite corrosion inhibitor on concrete is studied. This study involves the comparative studies of mechanical properties, durability properties of conventional concrete and high performance concrete in the case of without and with inhibitor. The grade of concrete used for this research work is M 30 for conventional concrete. The same grade is used for High performance concrete (HPC) by replacing cement with Ground Granulated Blast Furnace Slag (GGBS) by 40 percent and addition of silica fume by 4 percent based on earlier study. The mechanical properties and durability properties of concrete for four different mix namely ordinary and high performance concrete with (0.5, 1, 1.5 and 2percent) and without inhibitor were studied. Electrochemical measurements also studied by using Electrical field analyzer.

**Keywords-** Ground granulated blast furnace slag, Concrete, Calcium nitrite, Durability properties and Corrosion studies, Mechanical properties, Silica fume.

## I. INTRODUCTION

Since the early 1970s, corrosion has been recognized as a problem in reinforced concrete structures. In coastal environments, structures typically subject to corrosion are sea walls and piers, as well as bridge piles, girders, and decks. Corrosion in all of these types of structures is severe and widespread. Internal damage is caused by the corrosive action of external and internal chlorides on embedded reinforcing steel and prestressing strands in the concrete. The external chlorides are from de-icing salts, marine sea-spray, and immersion in water containing chlorides. Chlorides also enter concrete by means of construction materials such as marine aggregates; chloride contaminated mixing water, and chloride containing admixtures such as calcium chloride. When iron is exposed to water and oxygen, it oxidizes and produces a corrosion by-product (rust). This steel corrosion by-product can expand in size to approximately four times its original volume, creating tensile stresses within the concrete and causing the concrete to

crack and spall; this action allows chlorides to enter at an even faster rate. However, actual corrosion will not be evenly distributed, indicating that a much lower average percentage loss could result in cracking. Steel reinforced concrete is one of the most durable and cost effective construction materials but it can suffer in high chloride environments from corrosion due to chloride induced break down of the normal passive layer protection. To prevent or decelerate the corrosion process the following methods are commonly adopted,

- protective coatings,
- corrosion-resistant alloys,
- corrosion-inhibiting admixtures,
- engineering plastics and polymers, and
- cathodic and anodic protection

One way of protection embedded steel reinforcement from chloride induced corrosion is by the addition of corrosion inhibiting admixtures (CIA) to the concrete mixes

which is one of the most user-friendly and cost-effective solutions.

## II. CORROSION INHIBITOR

In general, reinforced concrete has proved to be successful in terms of both structural performance and durability. However, there are instances of premature failure of reinforced concrete components due to corrosion of the reinforcement. The two principal factors provoking corrosion are the ingress of chloride ions from de-icing salts or sea water and the reaction of the alkaline pore solution with carbon dioxide from the atmosphere, a process known as carbonation. Despite the huge demand a simple, cheap, and reliable technique which either protects the steel from corrosion or at least lowers its corrosion rate is still lacking. Over the past decade, however, the concrete repair industry has developed novel techniques that are claimed to prevent, or at least to reduce, the corrosion of steel in concrete. The use of these 'corrosion inhibitors' is of increasing interest as they can be used in reinforced concrete either as a preventative measure for new structures (as an addition to the mixing water) or as surface applied inhibitors for preventive and restorative purposes. Addition to the mixing water does not require any additional working steps and allows a simple handling of the inhibitor, unless it affects the properties of the cement paste adversely. Application from the concrete surface could be a

promising technique to protect existing structures from corrosion or to increase the lifetime of structures that already show corrosion attack. The application of inhibitors on the concrete surface requires the migration of the substance to the rebar where it has to reach a sufficiently high concentration to protect steel against corrosion or reduce the rate of ongoing corrosion.

Another point concerning the terminology of 'inhibitors' must be clarified:

A corrosion inhibitor prolongs the service life due to chemical/electrochemical interaction with the reinforcement. Any other substances that may prevent the onset of corrosion or reduce ongoing corrosion by surface treatment (e.g. hydrophobation) or by admixtures that reduce porosity of the concrete (e.g. fly ash, silica fume, waterproofing admixtures etc.) are not considered to be corrosion inhibitors. Most of the results published in the literature and reviewed recently are from laboratory studies involving solution experiments or relatively small mortar samples. Long term performance results are available for admixed inhibitors only, in particular calcium nitrite. Results from well documented field tests involving surface applied inhibitors are rare. There are, however, other difficulties in obtaining unambiguous, conclusive results on the performance of corrosion inhibitors on reinforced concrete structures:

- Most of the 'inhibitors' available under different trade names are blends of essentially unknown composition that could be changed without notice. This makes even laboratory experiments difficult.
- Sometimes the use of surface-applied inhibitors is recommended only in conjunction with other corrosion protection methods, such as hydrophobation of the surface, and it is then difficult to isolate the inhibitor performance.

Corrosion inhibitors prevent or delay the corrosion initiation in concrete. The most frequently used technique is addition of the inhibitors to the mixing water of concrete as admixtures for new structures in order to prevent or at least delay the onset of corrosion.

### Types

The three most common generic types of corrosion inhibiting admixture are:

- a) Calcium nitrite (normally contains a residual amount of calcium nitrate)
- b) Amino alcohols
- c) Amino alcohols blended with inorganic inhibitors

The calcium nitrite type has more than a 40 year history of use but has been used more or its accelerating than its corrosion inhibiting properties until recently. The amino alcohol types have been available for over 10 years but it is only recently that usage.

### Mechanism

The mechanism by which corrosion inhibitors operate is dependent on their chemical nature. Calcium nitrite based corrosion inhibitors convert or "oxidise" the ferrous oxide sites within the protective passive oxide layer into ferric oxide (+3 oxidation state) which is more stable and less reactive than the +2 oxidation state, ferrous oxide. When the chloride ions reach the ferric oxide layer, no reaction occurs – the steel is in a passive state. It is the anodic corrosion sites on the steel that are protected against the chloride attack and for these reason nitrites are called anodic inhibitors. It is important that sufficient nitrite is present to counter the chloride ions. The dosage of the admixture is therefore based on the predicted level of chloride at the steel over the design life of the structure. Amino alcohol based corrosion inhibitors coat the embedded steel with a monomolecular layer that keeps the chlorides ions away from the embedded steel. They also inhibit the reaction of oxygen and water at the cathodic sites on the steel which are an essential part of the corrosion process. As a result amino alcohols can be regarded as both anodic and cathodic inhibitors.

### Calcium Nitrite

Calcium Nitrite is a White or straw yellow powder. Calcium nitrite powder manufactured with high quality nitrous acid. Calcium nitrite has anti freezing properties and it easily deliquesces. Calcium nitrite may be employed in concrete and mortar admixtures to impart water repellency and to improve flow and release properties of the dry mix. Calcium nitrite is one of the corrosion inhibitor used in concrete. It is one of the green corrosion inhibitor which doesn't provide any adverse effect to concrete as well as surroundings. So calcium nitrite is used as corrosion inhibitor in this research work.

## III. OBJECTIVES

The main objectives of the present study are,

- To investigate the performance of calcium nitrite corrosion inhibitor in ordinary concrete and high performance concrete.
- To study the mechanical and durability properties of concrete when inhibitor used as admixtures in fresh concrete.
- The effect of inhibitor will compare conventional concrete with high performance concrete.

- To study the corrosion test in ordinary concrete and high performance concrete without and with inhibitor by casting the specimens.

**IV. METHODOLOGY**

- Investigation of material properties.
- A mix design is proposed to achieve desired characteristics strength of M 30.
- A mix proportioning to be done by conventional trial mixing approaches for desired slump value and strength. Casting the specimens of ordinary concrete and high performance concrete without and with inhibitor by use the successive mix ratio.
- Studying the characteristics of both concrete by compressive strength, split tensile strength, flexural strength and modulus of elasticity.
- Studying the durability properties.
- Studying the corrosion test.
- Analysis of test data.
- Comparison of the results of the ordinary concrete and high performance concrete in the case of without and with inhibitor.

**V. MATERIALS**

The constituents which used to make conventional and high performance concrete are cement, silica fume, GGBS, fine aggregate, coarse aggregate, super plasticizer, and water. The ingredients of concrete are shown in Figure1. The properties of material were found and the results were shown here.

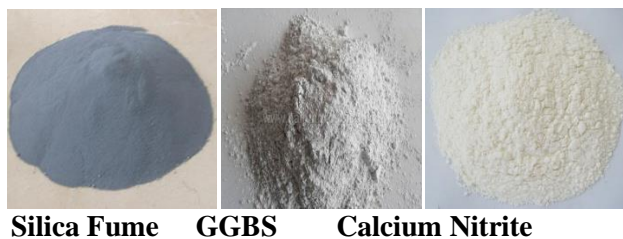


Fig 1 Ingredients of concrete

**Ordinary Portland Cement**

Now so widely available ordinary Portland cement is classified in to three grades namely, 33, 43, 53 grades depend on the strength of the cement at 28 days. For this research, OPC 43 grade of Zuari cement is used. The specific gravity of cement is 3.15 which determined by conduct the specific gravity test.

**Aggregates**

Fine aggregate and coarse aggregate are used in this research work. The sieve analysis tests were conducted and found the zone of sand. It is confirming to Zone II as per IS 383-1970 which shown in Figure 2. And 12.5mm size of coarse aggregate is used. The specific gravity of coarse aggregate and fine aggregate is 2.71 and 2.60 got from specific gravity test conducted.

**Silica Fume (SF)**

Silica fume, also known as micro silica, is an amorphous (non-crystalline) polymorph of silicon dioxide (SiO<sub>2</sub>). It is an ultra-fine powder collected as a byproduct of producing silicon metal or ferrosilicon alloys. The main field of application is as pozzolonic material for high performance concrete. So 4 percent of SF by mass of cement is added to attain high performance concrete. The specific gravity of silica fume is 2.0 to 2.4.

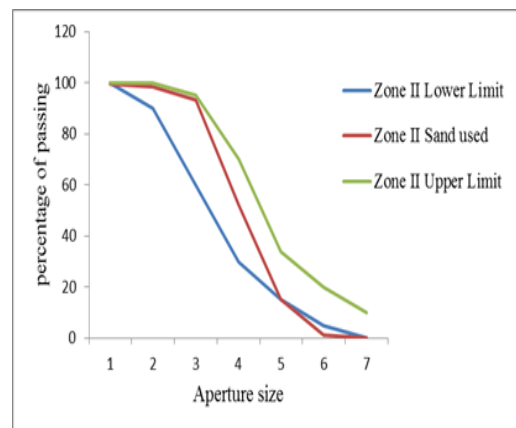


Fig 2. Zone II grade of sand

**Ground Granulated Blast Furnace Slag(GGBS)**

The chemical composition of GGBS is similar to that of cement clinker. The approximate chemical composition of GGBS is discussed in the Table 4.2. In this research work for high performance concrete 40 percent of

GGBS by mass of cement is replaced for cement content. The specific gravity of GGBS is 2.82 to 2.95.

**Water**

Ordinary tap water was used for mixing and curing all the specimens considered in this research.

**Super Plasticizers**

The Super Plasticizers are mainly used for achieving higher strength by reducing the water cement ratio or for improving workability. CONPLAST SP430 is used for this research work.

**Inhibitor – Calcium Nitrite**

In this research work calcium nitrite is used as a corrosion inhibitor in concrete. 0.5, 1, 1.5 and 2 percent of calcium nitrite by mass of cement weight is added in ordinary concrete and High performance concrete. The specific gravity of calcium nitrite is 1.30.

**VI. MIX PROPORTION**

The mix design should be done as per IS 10262 – 2009 for Ordinary concrete. The grade of concrete used for this research work is M 30 for conventional concrete. The same grade is used for High performance concrete (HPC) by replacing cement with Ground Granulated Blast Furnace Slag (GGBS) by 40 percent and 4 percent addition of silica fume. And the inhibitor is used in various percentage such as 0.5, 1.0, 1.5 and 2.0percent by mass of cement.

**Mix proportion for trial**

Proportion by weight

<b>C</b>	<b>: FA</b>	<b>: CA</b>	<b>: W/C</b>
450	: 687.5	: 1030.5	: 209
1	: 1.55	: 2.29	: 0.45

**VII. DESCRIPTION OF SPECIMENS**

The following notations going to be used for the without and with inhibitor concrete to identification of mix easily. The ordinary concrete (**OC**) and High performance concrete (**HPC**). In that above two concrete the various percentage of calcium Nitrite corrosion inhibitor were used. For that, the following symbols going to describe.

**NI** – No inhibitor

**I-1** – 0.5percent of Calcium nitrite inhibitor

**I-2** – 1.0 percent of Calcium nitrite inhibitor

**I-3** – 1.5 percent of Calcium nitrite inhibitor

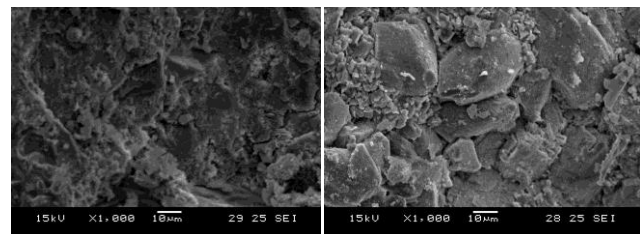
**I-4** – 2.0percent of Calcium nitrite inhibitor

**VIII. RESULTS AND DISCUSSION**

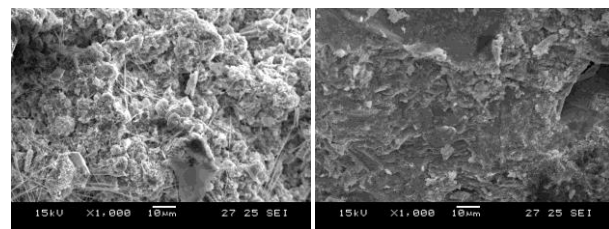
**SEM ANALYSIS**

A scanning electron microscope (SEM) is a type of electron microscope that produces images of a sample by scanning it with a focused beam of electrons. The electrons interact with electrons in the sample, producing various signals that can be detected and that contain information about the sample's surface topography and composition. The electron beam is generally scanned in a raster scan pattern, and the beam's position is combined with the detected signal to produce an image. SEM can achieve resolution better than 1 nanometer. Specimens can be observed in high vacuum, low vacuum and in environmental SEM specimens can be observed in wet conditions.

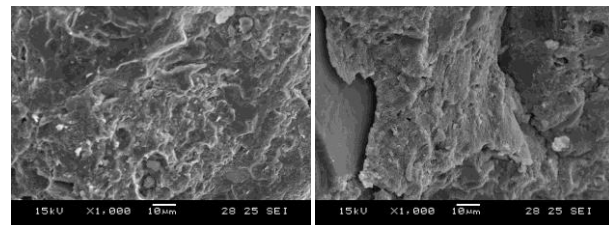
The SEM analysis views of without and with inhibitor concrete specimens is shown in figure 3. The 1000 magnification of SEM images are shown in figures.



*(a).OC without inhibitor Fig (b). HPC without inhibitor*



*Fig.(c ) OC with inhibitor Fig.(d) OC with inhibitor (0.5 percent) (2 percent)*



*Fig.(e)HPC with inhibitor Fig.(f) HPC with inhibitor (0.5 percent) (2 percent)*

*Fig 3.SEM analysis*

## STRENGTH TEST

### Compressive Strength test

From the compressive strength results of cubes and cylinders for various mixes it is observed that the specimens attain 70 percent of the compressive strength around the age of 7 days. The Compressive strength increases with increase in dosage of inhibitor. Comparative results of compressive strength of cubes and cylinders are shown in Figure 4(a) and 4(b).

### Compressive strength test results for cubes

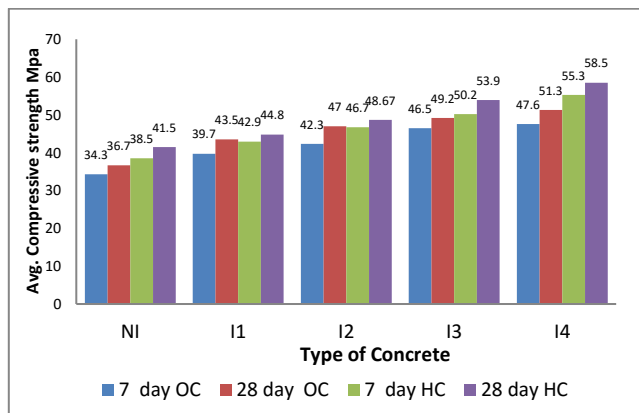


Fig (a) Compressive Strength of concrete cubes

### Compressive strength test results for cylinders

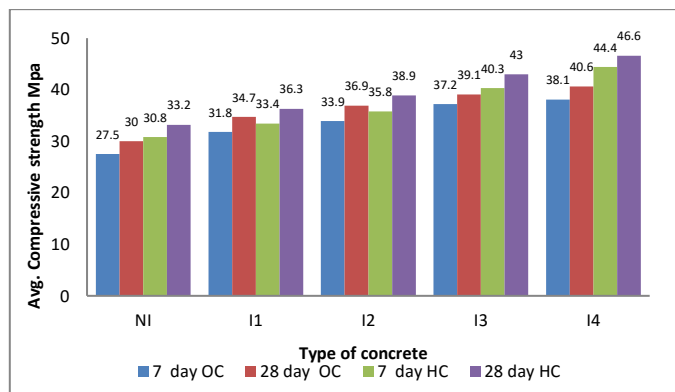


Fig 4(b) Compressive Strength of concrete cylinders

### Split Tensile Strength test

The results of the split tensile strength test carried out on the cylinders and corresponding result bar chart is shown in Fig 5. The Tensile strength increases with increase in dosage of inhibitor.

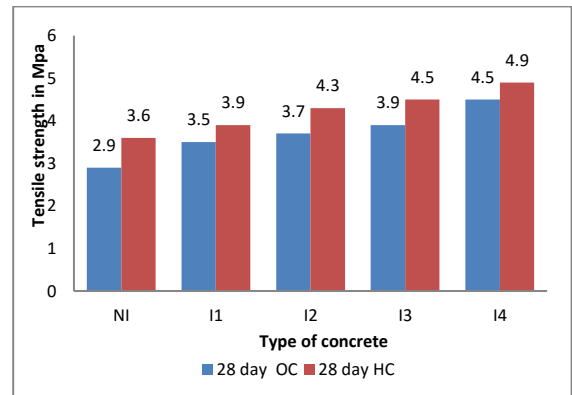


Fig 5 Split Tensile Strength of concrete cylinders

### Modulus of Elasticity of Concrete

The stress- strain curve for Modulus of Elasticity of concrete for 3 cylinders of size 150 mm diameter and 300 mm height is shown in the Figure 4.4. From the graph the corresponding E Values are calculated and the average of three cylinder values are considered as Modulus of Elasticity of concrete for all mixes. From IS 456-2000, the modulus of elasticity of M 30 grade of concrete can be assumed as follows

$$E_c = 5000 \sqrt{f_{ck}} \dots (1)$$

$$= 5000 \sqrt{30}$$

$$E_c = 2.7 \times 10^4 \text{ N/mm}^2.$$

The E value of various mixes in OC and HPC are found out. And the stress- strain graph for OC is shown in figure 6. It is seen from the result the addition of inhibitor performed better in both type of concrete

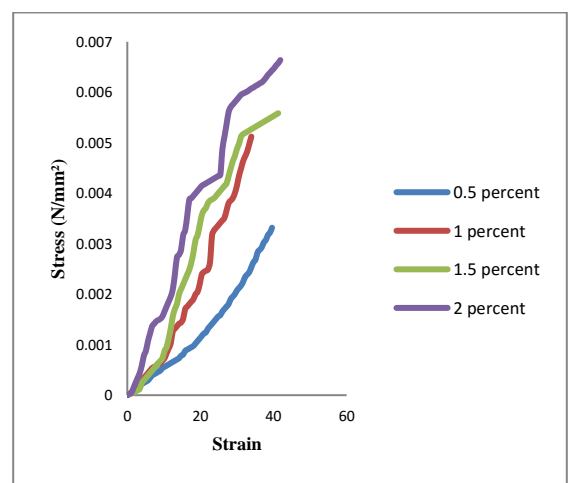
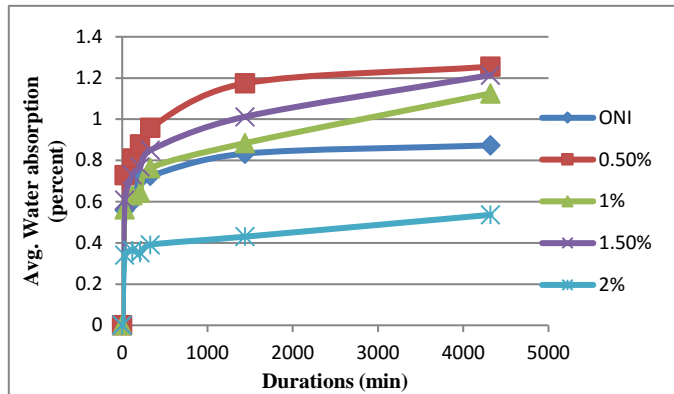


Fig 6 Graphs for Modulus of Elasticity for OC

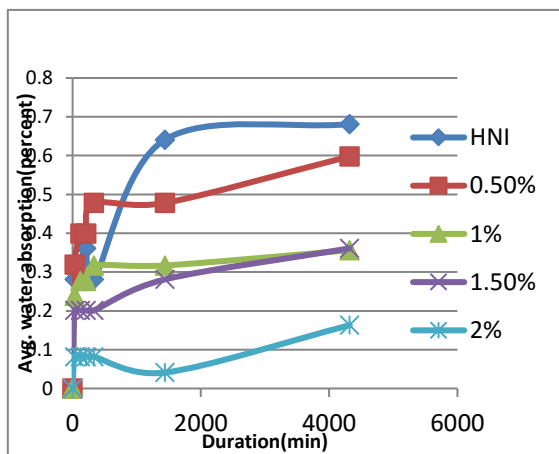
**DURABILITY TEST**

**Water absorption test**

According to ASTM C642 – 06, water absorption test was performed on cubes of size 100 mm. The test results of OC and HPC were analysed thoroughly and the respective graph is shown in figure 7 and figure 8. The result shows that addition of inhibitor provide better performance by absorb less amount of concrete.



*Fig 7 Water absorption in OC*



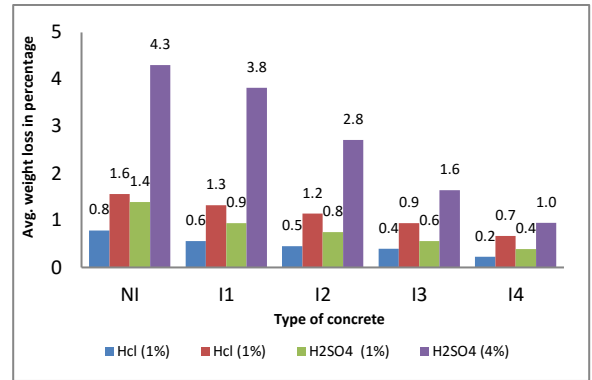
*Fig 8 Water absorption in HPC*

**Acid Resistance Test**

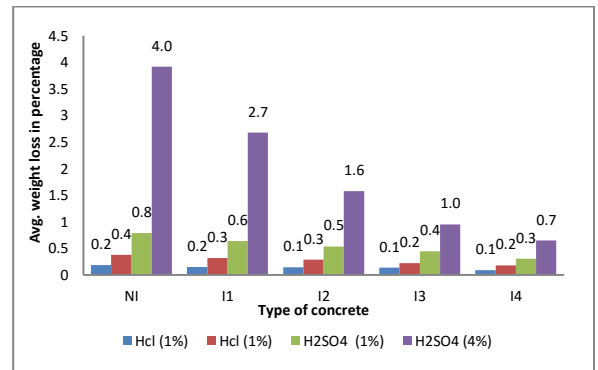
The acid resistance test was performed on cubes of size 100 mm. For this test two types of acid like HCl and H2SO4 were used at concentration like 1 and 4 percent. The specimens were immersed in acid up to 30 days then took out and found out the percentage of weight loss. The results were discussed through bar chart which is shown in figure 9 and figure 10. The up to 30 days then took out and found out the percentage of weight loss. The results were discussed through bar chart which is shown in figure 9 and figure 10. The result shows that addition of inhibitor provide better performance in acid attack.

**Rapid Chloride Permeability test**

The results of RCPT are given in table 1. The presence of inhibitor provides resistance to chloride permeability in concrete. The cumulative charge passed in coulombs was calculated by using the equation 3.5. And the results will be compared with ASTM standards to find the corrosion rate.



*Fig 9 Acid Resistance result for OC*



*Fig 10 Acid Resistance result for HPC*

**Table – 1 RCPT results**

Sl.no	Type of concrete	Charge passed (Coulombs) (Q)		Chloride permeability as per ASTM C 1202	
		OC	HPC	OC	HPC
1	NI	2741.4	2098.8	moderate	moderate
2	I1	547.2	216	Very low	Very low
3	I2	520.2	176.4	Very low	Very low
4	I3	480.6	140.4	Very low	Very low
5	I4	237.6	86.4	Very low	negligible

**Half - cell potential measurement**

By using the Canin corrosion meter the Half – cell potential measurements has been conducted. The test results for various types of concrete are given in table 2. The results which given in table are average of three samples.

**Table 2 Half - cell potential measurement results**

Sl.No.	Type of concrete	Potential range (mV)	Corrosion condition	
1.	OC	NI	-156	low
		I-1	-97	very low
		I-2	-79	very low
		I-3	-55	very low
		I-4	-19	Negligible
2.	HPC	NI	-133	Low
		I-1	-85	very low
		I-2	-58	very low
		I-3	-24	very low
		I-4	-15	Negligible

**Inference:**

When compared to without inhibitor concrete, with inhibitor concrete shows better results in corrosion condition. Increasing of dosage of inhibitor reduces corrosion risk in concrete. The corrosion condition is checked by using the ASTM C876 -2009.

**IX. CONCLUSIONS**

The following conclusions are drawn from the above research work:

- i. When the calcium nitrite used in concrete the strength of concrete is gradually increase when dosage increased in both ordinary and high performance concrete
- ii. In Durability studies the inhibitor shows good performance in chloride ion penetration, water absorption and acid resistance.
- iii. Similarly in corrosion test the inhibitor plays better performance when compared to without inhibitor concrete.

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## Standards

1. **ASTM C515 – 95** “Standard specification for chemical Resistant Ceramic Tower Packings.
2. **ASTM C642 – 13** “Standard Test Method for Density, Absorption, and Voids in Hardened Concrete.
3. **ASTM C876 – 09** “Standard Test Method for Corrosion Potentials of Uncoated Reinforcing Steel in Concrete.
4. **ASTM C1202 – 12** “Standard Test Method for Electrical indication of Concrete’s Ability to Resist Chloride Ion Penetration.
5. **IS 516-1959** “Methods of tests for strength of concrete”, Bureau of Indian Standards, New Delhi.
6. **IS 383-1970** “Specification for Coarse and Fine aggregates from natural sources for Concrete”, Bureau of Indian Standards, New Delhi.
7. **IS 10262-2009** “Concrete Mix Proportioning”, Bureau of Indian Standards, New Delhi.
8. **IS 456-2000** “Plain and reinforced Concrete - code of practice”, Bureau of Indian Standards, New Delhi.